

060301 Quiz 7 Morphology of Complex Materials

- 1) In class we discussed the source of the bell shaped curve of growth rate versus temperature.
 - a) Explain in words why a maximum in growth rate, G , is observed in temperature, T .
 - b) Write expressions for two rate constants k_d and k_g .
 - c) Derive a rate limiting function $G \sim 1/(1/k_d + 1/k_g)$ using the chemical kinetics model from class.
 - d) What are the two temperature limits for polymers in the growth rate curve?
 - e) Would you expect spherulites to follow such a bell shaped growth rate curve?

- 2) We also explored the Hoffman lamellar growth rate plot and function.
 - a) Give the Hoffman expression for lamellar growth rate G .
 - b) Explain what the terms are in this expression
 - c) Derive the two axes used in the Hoffmann plot.
 - d) Explain why this plot should be linear.
 - e) What is the relationship between the growth rate function of question 1 and the Hoffmann expression.

- 3) Hoffmann considered three regimes of spherulitic growth.
 - a) Describe the first regime.
 - b) Describe the second regime.
 - c) Describe the third regime.
 - d) Explain how the slope in the Hoffmann plot will vary with regime.
 - e) Criticize the Hoffman regime approach.

ANSWERS: 060301 Quiz 7 Morphology of Complex Materials

1a) The growth rate of a phase depends on two events, diffusion of the material which is forming the phase and conversion (surface nucleation) to the growing phase. The slower of these two rates governs the total rate. This is a classic rate limiting process. At high temperatures surface nucleation is slow and at low temperatures diffusion is slow. Between these two there is a maximum where nucleation isn't so slow and diffusion also isn't too bad.

b) $k_d \sim \exp(-U^*/kT)$ and $k_g \sim \exp(-E_g/kT)$

c) We have that the rate (1) $R = k_d [A] = k_g [B]$ and that (2) $C_f = A_i + B_i$ using (1) in (2) we have $C_f = A_i (1 + k_d/k_g)$ or that $A_i = k_g C_f / (k_g + k_d)$ if this is used in (1) we obtain:
 $R_i = k_d A_i = k_d k_g C_f / (k_d + k_g) = C_f / (1/k_d + 1/k_g)$

d) Glass transition and equilibrium melting points

e) Yes. The bell shaped rate limiting law works for all phase separations since all phase separations depend on a balance between nucleation and diffusion. (that is except for spinodal decomposition and phase separation in supercritical fluids I think off hand).

2) a) $G = \exp(-U^*/kT) \exp(-Df/kT)$

b) U^* is the activation energy for flow and Df is the free energy associated with a seed, $2\sigma t$ where σ is the surface energy and t is the lamellar thickness.

c) If we use the Hoffmann expression for t , $t = (2\sigma e / DH_f) (T_{inf} / (T_{inf} - T))$ we obtain
 $G = \exp(-U^*/kT) \exp(-4\sigma e \sigma T_{inf} / k(T(T_{inf} - T)))$

taking ln of both sides

$\ln G - U^*/kT = -4\sigma e \sigma T_{inf} / k(T(T_{inf} - T))$

The Hoffmann plot is the left function versus $T_{inf} / (T(T_{inf} - T))$

d) It is linear because the function is linear in these terms.

e) The Hoffmann law isn't rate limiting. It is a probability expression. The function will not show a maximum.

3) abc) The regimes are in the notes. In I $i \ll g$ and i rate limits growth $G \sim i$, in II $i \sim g$ and $G \sim i^{1/2}$. In III $i \gg g$ and growth is all seeds, $G \sim i$ again.

d) The slope in the Hoffmann plot is basically $\ln G$ so the slope in II is half the slope in I and in III since $\ln i^{1/2} = 1/2 \ln i$.

e) The problems with Hoffman are in the notes. Basically there isn't enough data to support the theory, it is difficult to access shallow quenches and deep quenches so data on I and III is mostly absent. The definition of U^* is weak. Several other issues were mentioned in the notes.